Direct Comparison of Arsenic Speciation in Coal Using XAFS Spectroscopy and a Sequential Leaching Protocol

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Beamline(s): **X18B**

Introduction: In this work, we demonstrate the value of combining a direct method (XAFS spectroscopy) and an indirect method (sequential leaching) for speciating an environmentally important element such as arsenic in coal. Such information is important in understanding how arsenic behaves during coal combustion and how its release to the environment might be minimized. The combination of the two methods provides more information than either method separately because the XAFS method can be used to confirm or reject the assumptions inherent in the leaching method, while the leaching method provides cleaner fractions for species identification by XAFS spectroscopy.

Methods and Materials: Arsenic XAFS spectroscopy was carried out at beam-line X-18B on the residues obtained from coals subjected to the 4-step leaching method developed at the U.S. Geological Survey (USGS) [1]. This procedure consists of leaching coal in first an ammonium acetate solution, then dilute hydrochloric acid, followed by hydrofluoric acid and finally by nitric acid. Each step is performed on 5g of pulverized coal for an 18-hour period at room temperature. XAFS spectra were collected using a 12-element germanium detector. A 6μ germanium filter and Soller slits were also used to enhance the signal/noise ratio. Instrumental neutron activation analysis (INAA) was used to determine concentrations of arsenic and other elements in the coal and in the residues after each leaching stage. Arsenic concentrations varied from 20 ppm to less than 1 ppm as the arsenic was progressively removed from the coal by the increasing severity of the leaching solutions.

Results: Figure 1 is an example of the unnormalized arsenic XANES spectra obtained from the residues of a coal progressively treated by the USGS leaching protocol. Such spectra do not have the effect of concentration removed from them, as is normally done in the XANES normalization procedure. Hence, the progressive removal of arsenic from the coal can be seen as the reduction in edge-step height of the spectra. When correlated with the concentration of arsenic in these residues measured by INAA, correlation coefficients (r^2) were found to exceed 0.95 for linear relationships between the edge-step normalization factors and the arsenic contents. In addition, the XANES spectra provide information on the arsenic forms removed by the leaching protocol at the different stages. In this case, the HCl treatment removes principally arsenate forms of As in the coal, as indicated by the disappearance of the peak at higher energy, the HF treatment has little, if any, effect, and the nitric acid treatment removes principally arsenic associated with pyrite. A small residue of arsenate remains after the four leaching treatments. The XANES spectra were then least-squares fitted using a procedure described elsewhere [2] in order to quantify the distribution of arsenic between the two major forms present in the coal. Such quantification confirmed that the HCl treatment removes only arsenate and the arsenic associated with pyrite was only removed by nitric acid. Further details of this investigation can be found elsewhere [3].

Conclusions: XAFS spectroscopy has provided valuable insight into the efficacy of a sequential leaching protocol designed for speciating arsenic and other trace elements in coal. Furthermore, such work shows that direct methods such as XAFS spectroscopy must be used to confirm the assumptions about elemental forms on which the indirect leaching methods are based in order to avoid incorrect conclusions.

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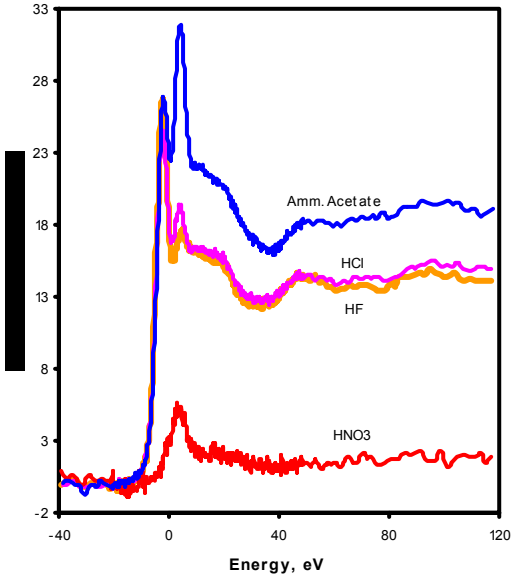

Figure 1. Unnormalized As XANES spectra obtained for a suite of coal residues after different stages of the leaching protocol [1]